Final Report
NASA Planetary Atmospheres Program
NAGW-3019
3/1/95 - 2/28/96

Laboratory Studies of Diacetylene and Cyanoacetylene Photochemistry: Routes to Complex Molecules in Titan and the Outer Planets' Atmospheres

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A. Summary of Progress

During the above grant period, we continued our experimental investigations of the photochemistry of diacetylene, which is thought to be a precursor to complex hydrocarbons in Titan's atmosphere. The chemistry of the diacetylene triplet metastable state ($C_4H_2^*$) with ethene, propene, and propyne in nitrogen and helium buffers was studied in a reaction tube attached to a pulsed nozzle. An ultraviolet photoexcitation laser counterpropagated the molecular expansion through a short reaction tube, exciting the C_4H_2 $^1\Delta_u \leftarrow ^1\Sigma_g^+$ $2^1_0 6^1_0$ and 6^1_0 transitions at 231.5 and 243.1 nm, respectively. Efficient intersystem crossing forms the metastable triplet state from which reaction occurs. The short length of the tube (8 mm) serves to quench the reaction after 10-30 microseconds so that primary products and not polymer are formed. Upon exiting the reaction tube, the photochemical products were soft ionized with 118 nm vacuum ultraviolet light and mass-analyzed in a linear time-of-flight mass spectrometer. The primary products in the reactions with ethene (C_6H_4, C_6H_5), propene (C_5H_5, C_5H_6, C_6H_4, and C_7H_6), and propyne (C_5H_3, C_5H_4, C_6H_2, and C_7H_4) are consistent with poly-yne, enyne, and cumulene products. Percent product yields are determined assuming equal photoionization cross sections for the products. Relative photoionization cross sections for a series of model alkene, alkyne, enyne, diene and diyne compounds were determined to test the variations in photoionization cross section expected for the products. Relative rate constants for the reactions (scaled to $k(C_4H_2^* + C_4H_2) = 1.00$) with ethene, propene, and propyne are extracted from concentration studies, determining values of 0.24 ± .01, 0.32 ± .01, and 0.42 ±.02 in helium buffer, respectively. Isotopic studies employing deuterated reactants are used to constrain the mechanisms for the reactions. Most of the major products are proposed to follow formation of an unbranched or branched chain adduct which subsequently decomposes by loss of interior atoms to form a stable poly-yne or en-yne product. Based on our data, we proposed two schemes

are proposed to account for formation of the isotopically labelled C_5H_4 and C_5H_3 products in the $C_4H_2^*$ + CH_3C_2H reaction. Only one of these mechanisms appears to be operative in the $C_4H_2^*$ + $CH_3CH{=}CH_2$ reaction.

Based on the experimental work, we carried out an estimate (in collaboration with Mark Allen, JPL) of the relative efficiencies of metastable diacetylene for forming larger hydrocarbons versus free radical processes. We have concluded that metastable diacetylene reactions can compete with free radical processes at lower altitudes. However, many of the rate coefficients needed to make a firm estimate still need to be measured.